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(54) [Title of the invention]

PRODUCTION PROCESS OF HEAT-SENSITIVE RECORDING SHEET

(57) [Abstract]

[Object] To provide a heat-sensitive recording sheet which is excellent in image quality, glossiness and image clarity as well as in recording characteristics.

[Constitution] A process comprising: forming, on a heat-sensitive coloring layer, an inner coating layer containing an electron beam-curable unsaturated organic compound; forming, on a highly smooth shaping surface, an outer coating layer containing a white pigment and an electron beam-curable unsaturated organic compound; bringing the inner coating layer with the outer coating layer into close contact; curing the resulting laminate by irradiation with an electron beam to thereby completely unify the inner coating layer with the outer coating layer; and releasing the formed gloss layer from the shaping surface.

[Claims]

[Claim 1] A process for producing a heat-sensitive recording sheet, comprising the steps of providing a heat-sensitive coloring layer on at least one side of a substrate, optionally providing an intermediate layer on the heat-sensitive coloring layer, and forming an electron beam-curable gloss layer on the heat-sensitive coloring layer or on the intermediate layer, characterized in that the step of forming the electron-beam curable gloss layer comprises the steps of:

applying, to the heat-sensitive coloring layer, or to the intermediate layer, a coating composition containing an unsaturated organic compound curable by irradiation with an electron beam to thereby form an inner coating layer;

applying, to a shaping surface with high smoothness, a coating composition containing as main constituents a white pigment (A) and an electron beam-curable unsaturated organic compound (B) in such proportions that the weight ratio A/B is 40/60 to 95/5 to thereby form an outer coating layer;

optionally subjecting the formed outer coating layer to a predrying and to an irradiation with an electron beam;

bringing the outer coating layer into close contact with the inner coating layer to thereby form a gloss layer

composed of the outer coating layer and the inner coating layer;

curing the formed gloss layer by irradiation with an electron beam to thereby completely unify the outer  
5 coating layer with the inner coating layer;

and releasing the resultant gloss layer from the shaping surface.

[Detailed Description of the Invention]

[0001]

10 [Field of Industrial Application]

The present invention relates to a heat-sensitive recording sheet, more specifically to a heat-sensitive recording sheet which provides recorded images that are excellent in image quality, glossiness and image  
15 clarity, as well as excellent recording characteristics.

[0002]

[Prior Art]

Heat-sensitive recording sheets generally comprise a support made of paper, synthetic paper, plastic  
20 film or the like, and a heat-sensitive coloring layer formed on one side of the support and containing as main constituents a colorless or pale-colored coloring substance such as electron-donating leuco dye, an organic acidic developer such as an electron-accepting phenol  
25 compound, and a binder. The color-forming dye is reacted

with the developer upon application of thermal energy to  
thereby form a colored recorded image. Such recording  
sheets have advantages in that recording devices used  
therefor are compact, inexpensive and easy to maintain,  
5 and thus are in extensive use not only as recording media  
for facsimile machines, ticket-vending machines,  
scientific measuring instruments and so on, but also as  
output media in printers or plotters for POS labels, CAD,  
CRT medical images or the like.

10 [0003]

Among them, for use in image printers in CRT  
medical measuring instruments which require uniformity and  
high resolution in recorded images and for use in CAD  
plotters which require dimensional stability and fine-line  
15 recording, heat-sensitive recording sheets which comprise  
as a substrate synthetic paper of multi-layer structure or  
a biaxially oriented thermoplastic resin film optionally  
containing an inorganic pigment are used. For high value-  
added heat-sensitive recording sheets, such as video  
20 printer paper, not only high image quality, but also  
enhanced glossiness and image clarity are demanded.  
However, in order to achieve enhanced glossiness and image  
clarity as well as excellent quality in recorded images,  
such as high uniformity and resolution, it is necessary to  
25 improve the texture and cushioning characteristics of the

substrate and additionally to impart high smoothness to the outermost layer of the heat-sensitive recording sheet.

[0004]

One known method disclosed in Japanese  
5 Unexamined Patent Publication No. 1987-279980 is to use a coating composition that is curable with an ultra-violet beam or an electron beam in order to impart high smoothness to the outermost layer of a heat-sensitive recording sheet. While this method gave high glossiness,  
10 it generated rippling on the surface due to shrinking during curing, thus interfering with image clarity, and resulting in unsatisfactory quality.

[0005]

On the other hand, technical problems are  
15 pointed out regarding the above method, that is, the high smoothness imparted to the outermost layer of the heat-sensitive recording sheet increases the contact area between a thermal recording head and the outermost layer, so that the thermal recording head leaves its running  
20 trace on the outermost layer or grinds the outermost layer, producing grinding debris which will adhere to the thermal recording head, thereby greatly obstructing proper recording and, additionally, the increased likelihood of the head becoming adhered to the outermost layer under  
25 high humidity conditions leads to improper advance of the

recording sheet.

[0006]

An object of the present invention is to solve the aforementioned problems associated with the prior art  
5 heat-sensitive recording sheets and provide a heat-sensitive recording sheet which is excellent in image quality, glossiness and image clarity as well as in recording characteristics.

[0007]

10 The present inventors conducted extensive research to achieve the above object and formerly filed Japanese Patent Application No. 1993-202039 based on the finding that a gloss layer which is absolutely free of rippling due to shrinking during curing can be produced  
15 either by applying onto a substrate heat-sensitive coloring layer, or onto an intermediate layer when such an intermediate layer is provided on the heat-sensitive coloring layer, a coating composition comprising as the main component an unsaturated organic compound curable by  
20 irradiation with an electron beam, bringing the resulting coating into close contact with a shaping surface having high smoothness, curing the coating with an electron beam, and then releasing the resulting layer from the shaping surface to thereby transfer the high smoothness of the  
25 shaping surface to the gloss layer cured by the electron

beam; or by applying the coating composition onto the shaping surface, laminating the resulting coating with a substrate heat-sensitive coloring layer, or with an intermediate layer when such an intermediate layer is provided on the heat-sensitive coloring layer, curing the coating with an electron beam, and then releasing the resulting layer from the shaping surface to thereby transfer the high smoothness of the shaping surface to the gloss layer cured by the electron beam. The above processes enabled the production of a heat-sensitive recording sheet with excellent glossiness and image clarity.

[0008]

However, it was found later that, in order to also improve the recording characteristics by preventing recording problems, improper advance of the recording sheet, etc., it is effective that a large amount of a white pigment be contained so that the hardness of the coating film can be increased, thus reducing the deformation of the gloss layer caused by the thermal recording head, and that an oligomer be used as a main constituent so that the toughness of the electron beam-cured coating film can be increased, thus reducing the abrasion of the outermost layer caused by the thermal recording head.

[0009]

Accordingly, the present inventors carried out extensive research to achieve the above-described improvement, and found that by applying a coating  
5 composition comprising as main components an unsaturated organic compound curable by irradiation with an electron beam and a large amount of a white pigment to a shaping surface with high smoothness to thereby form an outer coating layer, subjecting the formed outer coating layer  
10 to a predrying and to an irradiation with an electron beam if necessary, bringing the outer coating layer into close contact with an inner coating layer mainly comprising an unsaturated organic compound curable with an electron beam and formed on a heat-sensitive coloring layer or on an  
15 intermediate layer for the purpose of facilitating easy release of the outer coating layer from the shaping surface and enhancing the adhesion of the outer coating layer to the heat-sensitive coloring layer or to the intermediate layer, curing the formed gloss layer composed  
20 of the outer coating layer and the inner coating layer by irradiation with an electron beam to thereby completely unify the outer coating layer with the inner coating layer, and releasing the gloss layer from the shaping surface to thereby transfer the high smoothness of the highly smooth  
25 shaping surface to the surface of the gloss layer cured by



the electron beam, the problem of rippling due to shrinking during curing is totally eliminated, whereby excellent glossiness and image clarity are imparted. The present inventors also found that the hardness and toughness of the cured coating film thus improved lead to solve the recording problems and improper advance, thereby improving the recording characteristics. The present invention was accomplished based on these findings.

[0010]

10           The present invention provides a process for producing a heat-sensitive recording sheet, comprising the steps of providing a heat-sensitive coloring layer on at least one side of a substrate, optionally providing an intermediate layer on the heat-sensitive coloring layer, and forming an electron beam-curable gloss layer on the heat-sensitive coloring layer or the intermediate layer, characterized in that the step of forming the electron-beam curable gloss layer comprises the steps of applying, to the heat-sensitive coloring layer, or to the intermediate layer, a coating composition containing an unsaturated organic compound curable by irradiation with an electron beam to thereby form an inner coating layer, applying, to a shaping surface with high smoothness, a coating composition containing as main constituents a white pigment (A) and an electron beam-curable unsaturated

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organic compound (B) in such proportions that the weight ratio A/B is 40/60 to 95/5 to thereby form an outer coating layer, optionally subjecting the formed outer coating layer to a predrying and to an irradiation with an electron beam, bringing the outer coating layer into close contact with the inner coating layer to thereby form a gloss layer composed of the outer coating layer and the inner coating layer, curing the formed gloss layer by irradiation with an electron beam to thereby completely unify the outer coating layer with the inner coating layer, and releasing the resultant gloss layer from the shaping surface.

[0011]

The process of the present invention will be described below with reference to the drawings. Figs. 1 and 2 are schematic illustrations of examples of an apparatus usable in the present invention. Fig. 1 shows the sequence of steps to be followed to perform the process of the invention, in which, by using a metal cylindrical rotator as a highly smooth shaping surface, an outer coating layer coating composition mainly comprising a white pigment and an electron beam-curable unsaturated organic compound is preliminary applied to the metal cylindrical rotator to thereby form an outer coating layer on the rotator, another coating composition mainly

comprising an electron beam-curable unsaturated organic compound is applied to a sheet substrate to thereby form an inner coating layer, the formed inner coating layer is brought into close contact with the white-pigment-

5 containing outer coating layer formed on the metal cylindrical rotator to thereby form a gloss layer having a laminated structure, the formed gloss layer is cured by irradiation with an electron beam to thereby completely unify the inner coating layer with the outer coating layer,  
10 and the resultant gloss layer is released from the metal cylindrical rotator.

[0012]

According to Fig. 1, a first coating composition 9, placed in a first coating composition container 8, is  
15 applied to the back surface of the sheet substrate 11 running in the direction of the arrow with a first coater 10 suitably selected, such as an offset gravure coater, thereby forming a first coating layer 12.

[0013]

20 Subsequently, as the metal cylindrical rotator 5 of a curing facility 1 runs in the direction of the arrow, coating layers are formed, dried and laminated around the peripheral surface of the rotator. More specifically, a second coating composition 3, placed in a second coating  
25 composition container 2 arranged so as to face towards the

peripheral surface of the rotator 5, is applied to a shaping surface of the rotator with a second coater 4, such as an offset gravure coater, to thereby form a second coating layer 7a. The second coating layer 7a may, if  
5 desired, be predried by a dryer 6' that uses infrared rays and/or hot air, thereby forming a dried second coating layer 7'. Further, if required, the dried second coating layer 7' may be irradiated with an electron beam using a first electron beam irradiator 6, thereby forming a cured  
10 second coating layer 7b. The second coating layer 7a, the dried second coating layer 7' and the cured second coating layer 7b are hereinafter collectively referred to as a second coating layer 7.

[0014]

15 In the following step, the sheet substrate 11, having the first coating layer 12 formed thereon, is guided onto the peripheral surface of the rotator 5 by a guide roll 13, by which the first coating layer 12 is brought into close contact with the second coating layer 7  
20 formed on the shaping surface, thus forming a gloss layer having a laminated structure composed of the first coating layer 12 and the second coating layer 7. Then, the gloss layer is irradiated with an electron beam through the sheet substrate 11 using a second electron beam irradiator  
25 14, thereby curing the gloss layer and ultimately

completely unifying the laminated layers, whereby a heat-sensitive recording sheet 16 is obtained. The obtained heat-sensitive recording sheet is released from the rotator 5 by a releasing roll 15 and taken up.

5 [0015]

According to the production process of heat-sensitive recording sheet of the present invention shown in Fig. 2, instead of the rotator 5 of Fig. 1, one surface of a running sheet material 17 is used as a shaping  
10 surface on which to form, dry and laminate an outer coating layer. In Fig. 2, a second coating composition 3, placed in a second coating composition container 2, is applied to one surface of the sheet material 17 running in the direction of the arrow with a second coater 4, thereby  
15 forming a second coating layer 7a. The second coating layer 7a may, if desired, be predried by a dryer 6' that uses infrared rays and/or hot air, thereby forming a dried second coating layer 7'. Further, if required, the dried second coating layer 7' may be irradiated with an electron  
20 beam using a first electron beam irradiator 6, thereby forming a cured second coating layer 7b. The second coating layer 7a, the dried second coating layer 7' and the cured second coating layer 7b are hereinafter collectively referred to as a second coating layer 7.

25 [0016]

The second coating layer 7 formed on the sheet material 17 is brought into close contact with a first coating layer 12 formed on a sheet substrate 11 by a guide roll 13, thereby forming a gloss layer having a laminated structure composed of the second coating layer 7 and the first coating layer 12. The gloss layer is then irradiated with an electron beam through the sheet material 17 using a second electron beam irradiator 14, thereby curing the gloss layer and ultimately completely unifying the laminated layers, whereby a heat-sensitive recording sheet 16 is obtained. The obtained heat-sensitive recording sheet is released from the sheet material 17 by means of releasing rolls 15 and taken up.

[0017]

In the case where a sheet material is used as a shaping surface, it is also possible to locate both of a first electron beam irradiator and a second electron beam irradiator at the side opposite to that shown in Fig. 2. In addition, it is required that both the peripheral velocity of the metal cylindrical rotator 5 shown in Fig. 1 and the running speed of the sheet material 17 shown in Fig. 2 be set to the same as the running speed of the sheet substrate 11. Although the material and shape of the metal cylindrical rotator are not particularly limited, it is preferred the rotator be made of stainless steel,

copper, chrome or the like and have a mirror finished smooth surface. Also, if necessary, a release agent, such as silicone oil or wax, may be applied to the surface of the rotator in advance in order to facilitate easy release  
5 of the cured gloss layer.

[0018]

The material and shape of the sheet material shown in Fig. 2 are not limited. However, it is suitable that the sheet material be made of a plastic sheet, a  
10 metallic foil such as an aluminum foil, etc., and have high smoothness and a relatively small thickness. A sheet material with a large thickness lacks in flexibility and tends to bend during the course of laminating or releasing. If required, a release agent, such as silicone oil or wax,  
15 may be applied to the surface of the sheet material in advance in order to facilitate easy release of the cured gloss layer. Further, the sheet material may be processed into an endless belt before use.

[0019]

20 Electron-beam accelerators for use in electron beam irradiation are not limited and include, for example, electron-curtain type, scanning type and like electron beam irradiators. Among them, those of electron-curtain type which are inexpensive and capable of obtaining high  
25 output can be effectively used. An electron beam is

irradiated at an accelerating voltage of preferably 100 kV or higher. In order to minimize the damage to the substrate, it is preferred that the curing be successfully accomplished with a minimum absorption dosage of the  
5 electron beam.

[0020]

Examples of the substrate to be used in the present invention include synthetic paper prepared by heating and kneading a polyolefin resin and a white  
10 inorganic pigment, extruding the melt from a die, stretching the extrudate in the longitudinal direction, laminating one or two layers of a film formed from a polyolefin resin and a white inorganic pigment on both sides of the longitudinally stretched film, and stretching  
15 the obtained laminated film in the transverse direction to make the film translucent or opaque. Further examples include a film formed by heating and kneading polyethylene, polypropylene, an ethylene-vinyl acetate copolymer resin, polyvinyl chloride, polystyrene, polyester or like  
20 thermoplastic resin either singly or in combination, extruding the melt from a die and biaxially stretching the extrudate; an opaque film formed from a mixture of the above-exemplified resin and a white inorganic pigment by biaxial stretching; and a paper made of pulp fibers such  
25 as wood-free paper, mechanical paper, roll paper, recycled



paper, coated paper and the like. A support made of pulp fibers, when used, is preferably provided thereon with a coating layer before being provided with a heat-sensitive layer in order to improve the uniformity of the images.

5 [0021]

The heat-sensitive coloring layer according to the present invention can be formed by applying a heat-sensitive coloring layer coating composition which mainly comprises a colorless or pale-colored electron-donating  
10 leuco dye, an organic acidic substance that causes the leuco dye to develop a color by application of heat, and a binder, and which optionally comprises a cross-linking agent, a pigment, or a heat-fusible substance. It is generally preferred, from the viewpoint of coloring  
15 sensitivity and color density, that the coating amount of the heat-sensitive coloring layer be 3 to 15 g/m<sup>2</sup> after drying.

[0022]

The coating may be performed using a technique  
20 generally employed by those skilled in the art, such as air knife coating, Meyer bar coating, blade coating, reverse roll coating or slit die coating. The surface of the heat-sensitive coloring layer may be subjected to a smoothing treatment, for example, with a super calender,  
25 gloss calender, machine calender or the like, in order to

improve the coatability and thereby enhance the recording density and sensitivity.

[0023]

As the color-forming dye, a colorless or pale-colored electron-donating leuco dye that reacts with the developer upon heating to develop a color is used. The color-forming dye usable in the present invention includes, for example, at least one member selected from the group consisting of 2,2-bis{4-[6'-(N-cyclohexyl-N-methylamino)-3'-methylspiro(phthalide-3,9'-xanthene)-2'-ylamide]phenyl}propane, 3-diethylamino-6-methyl-7-anilinofluoran, 3-piperidino-6-methyl-7-anilinofluoran, 3-(N-methyl-N-cyclohexyl)amino-6-methyl-7-anilinofluoran, 3-dimethylamino-7-chloroanilinofluoran, 3-[N-ethyl-N-(p-methylphenyl)amino]-6-methyl-7-anilinofluoran, 3-diethylamino-7-(metatrifluoromethyl)anilinofluoran, 3-(N-ethyl-N-tetrahydrofurfuryl)amino-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isopentyl)amino-6-methyl-7-anilinofluoran, 3-(N,N-dibutyl)amino-6-methyl-7-anilinofluoran and like fluoran-based dyes.

[0024]

The developer used in the present invention comprises an electron-accepting organic acidic substance that reacts with the color-forming dye upon heating to thereby develop a color. The developer is liquefied or

evaporated at room temperature or higher, preferably 70°C or higher, so that it can react with the color-forming dye, thereby causing the dye to develop a color. The developer is generally used in an amount of 1 to 5 weight parts, preferably 1.5 to 3 weight parts, per weight part of the color-forming dye in order to maximize the color density.

[0025]

The developer includes, for example, at least one member selected from the group consisting of 4,4'-isopropylidenediphenol (bisphenol A), 4,4'-isopropylidenebis(2-chlorophenol), 4,4'-isopropylidenebis(2-methylphenol), 4,4'-isopropylidenebis(2,6-t-butylphenol), 4,4'-sec-butylidenediphenol, 4,4'-cyclohexylidenediphenol, 4-t-butylphenol, 4-phenylphenol, 4-hydroxydiphenoxide, 4,4'-dihydroxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone, 3,3'-dihydroxydiphenylsulfone, 3,3'-diamino-4,4'-dihydroxydiphenylsulfone, 3,3'-diallyl-4,4'-dihydroxydiphenylsulfone, 3,3'-dichloro-4,4'-dihydroxydiphenylsulfone, 4-hydroxydiphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, 4-hydroxy-4'-benzyloxydiphenylsulfone, 2,4-dihydroxydiphenylsulfone, 2,4-dihydroxy-4'-methyldiphenylsulfone and 3,4-dihydroxyphenyl-p-tolylsulfone.

[0026]

According to the present invention, the heat-sensitive coloring layer may contain either a water-soluble resin or a water-dispersible resin as the binder. Examples are water-soluble resins such as polyvinyl alcohol, starch, modified starch, gum arabic, gelatin, casein, chitosan, methyl cellulose, hydroxy methycellulose, hydroxy ethylcellulose, polyvinyl pyrrolidone, polyacrylic acid salt, polyacrylamide, polyester resins, styrene-acrylate copolymer resins, styrene-maleic anhydride copolymer resins, methylvinylether-maleic anhydride copolymer resins and isopropylene-maleic anhydride copolymer resins, and water-dispersible resins such as vinyl acetate emulsion, acrylate copolymer emulsion, methacrylate copolymer emulsion, polyurethane emulsion, polyvinyl chloride emulsion, SBR latex, MBR latex and like emulsions having a good film-forming ability, i.e., a minimum film-forming temperature of 20°C or lower. These resins can be used singly or in combination.

[0027]

It is, however, important to assure that the mixture, which is obtained by mixing the binder with a dispersion of each of the color-forming dye and the developer, does not develop a color, coagulate or exhibit high viscosity, and that the formed heat-sensitive recording layer film is tough and free from

desensitization. Preferably, the binder is contained in the heat-sensitive coloring layer in an amount of 8 to 20% by weight based on the weight of the solids of the heat-sensitive coloring layer. An amount of less than 8% by weight decreases the strength of the coating film, while an amount of more than 20% by weight deteriorates the sensitivity.

[0028]

The heat-sensitive coloring layer may also contain a cross-linking agent for curing resins for the purpose of increasing its water resistance. Examples of the cross-linking agent include glyoxal, dialdehyde starch, glutaraldehyde and like dialdehyde compounds, polyethyleneimine and like polyamine compounds, epoxy compounds, polyamide resins, melamine resins, glyceringlycidylether and like diglycidyl compounds, dimethylolurea compounds, aziridine compounds, block isocyanate compounds, ammonium persulfate, ferric chloride, magnesium chloride, sodium tetraborate, potassium tetraborate and like inorganic compounds, boric acid, boric acid triesters, boron-based polymers, etc. The cross-linking agent may be used in an amount of 1 to 10% by weight based on the weight of the solids of the heat-sensitive coloring layer.

[0029]

The heat-sensitive coloring layer may further contain, in order to prevent stinking and generation of residual substances, a finely powdered pigment which has high whiteness and an average particle size of 5  $\mu$ m or  
5 smaller. Examples of such pigments include inorganic pigments such as calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcined clay, silica, diatomaceous earth, synthetic aluminum silicate, zinc oxide, titanium oxide, aluminum hydroxide, barium sulfate and surface-  
10 treated calcium carbonate and silica; and organic pigments such as urea-formalin resins, styrene-methacrylic acid copolymer resins and polystyrene resins. Preferably, the pigment is contained in an amount of 40% by weight or less based on the weight of the solids of the heat-sensitive  
15 coloring layer so as to prevent a reduction in color density.

[0030]

Examples of usable heat-fusible substances include stearic acid amide, stearic acid bisamide,  
20 oleamide, palmitic acid amide, cocamide, behenamide and like fatty acid amides, zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax, ester wax and like waxes (or lubricants), dimethyl terephthalate, dibutyl terephthalate, dibenzyl terephthalate, dibutyl  
25 isophthalate, phenyl 1-hydroxynaphthoate, 1,2-di(3-

methylphenoxy)ethane, 1,2-diphenoxyethane, 1-phenoxy-2-(4-methylphenoxy)ethane, diphenyl carbonate, p-benzylbiphenyl, 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-butylidenebis(6-t-butyl-3-methylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 2,4-di-t-butyl-3-methylphenol, 4,4'-thiobis(3-methyl-6-t-butylphenol) and like hindered phenols, 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-hydroxy-4-benzyloxybenzophenone and like sensitizers, antioxidants and UV absorbers.

[0031]

Generally, it is preferred that the heat-fusible substance be contained in the heat-sensitive coloring layer in an amount of 4 weight parts or less per weight part of the developer. For the purpose of improving the wetting property of the heat-sensitive coloring layer coating composition and preventing fish eyes in the coating, it is possible to further add a wetting property improver such as acetylene glycol or dialkyl sulfosuccinate, a dispersing agent for pigment, a defoaming agent, a fluorescent dye and the like.

[0032]

In the heat-sensitive recording sheet of the present invention, it is effective to provide an

intermediate layer between the heat-sensitive coloring layer and the gloss layer from the standpoint of ensuring adhesion between the heat-sensitive coloring layer and the gloss layer, preventing the fogging which is apt to occur during the application or curing of the gloss layer, etc. The intermediate layer can be formed by applying, onto the heat-sensitive coloring layer, a coating composition comprising as main constituents a water-soluble and/or a water-dispersible resin, a pigment, a lubricant and a cross-linking agent such that the coating amount after drying is 1.0 to 5.0 g/m<sup>2</sup>. A coating amount of less than 1.0 g/m<sup>2</sup> results in a coating film unevenly formed and having pinholes and defects, thus leading to degraded image quality and surface characteristics. On the other hand, a coating amount exceeding 5.0 g/m<sup>2</sup> results in decreased sensitivity and therefore lowered recording density. The coating may be performed by the same method as that employed for the formation of the heat-sensitive coloring layer.

20 [0033]

In order to facilitate the formation of the gloss layer and to thereby improve the recording density, sensitivity and glossiness, the surface of the intermediate layer may be subjected to a smoothing treatment with a super calender, gloss calender, machine

25



calender or the like. The amount of the resin to be contained in the intermediate layer is preferably 20 to 80% by weight based on the weight of the solids of the intermediate layer. The amount of the pigment to be  
5 contained in the intermediate layer is 20 to 80% by weight based on the weight of the solids of the intermediate layer. If the resin is contained in an amount of more than 80% by weight, sticking may be caused during recording. If the resin is contained in an amount of less  
10 than 20% by weight, the barrier property of the coating film is degraded, thereby causing fogging and, additionally, the ability to prevent penetration of the inner coating layer coating composition is decreased, ultimately failing to strengthen the adhesion between the  
15 heat-sensitive coloring layer and the gloss layer. The resin, pigment, lubricant and cross-linking agent to be used in the intermediate layer may be suitably selected from those used for the heat-sensitive coloring layer.

[0034]

20 The outer coating layer, which forms a part of the gloss layer of the invention, may be formed by applying a coating composition which comprises as main constituents a white pigment (A) and an electron beam-curable unsaturated organic compound (B) in such  
25 proportions that the weight ratio A/B is 40/60 to 95/5, in

such a manner that the coating amount after drying is 1.0 to 10.0 g/m<sup>2</sup>. If the coating amount is more than 10.0 g/m<sup>2</sup>, the sensitivity is deteriorated and, even with the help of an increased coating amount of the heat-sensitive coloring layer, the recording density is decreased. If the coating amount is less than 1.0 g/m<sup>2</sup>, the releasability from the shaping surface after curing is degraded and, further, high image clarity and glossiness are not likely to be achieved.

10 [0035]

It is preferred that the white pigment be contained in an amount as large as possible from the standpoint of enhancing the hardness of the cured coating film. More preferably, the proportion of the white pigment is selected such that the weight ratio A/B is 95/5 or less for achieving high releasability from the shaping surface and providing excellent surface characteristics in the cured coating film, or such that the weight ratio A/B is 40/60 or more for bringing about the desired hardness.

20 [0036]

The outer coating layer, which forms a part of the gloss layer of the invention, may contain a finely powdered pigment which has high whiteness and an average particle size of 5  $\mu$ m or smaller in order to increase its hardness and whiteness and to decrease recording problems

and improper advance of the recording sheet. Examples of such pigments include inorganic pigments such as calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcined clay, silica, diatomaceous earth, synthetic  
5 aluminum silicate, zinc oxide, titanium oxide, aluminum hydroxide, barium sulfate and surface-treated calcium carbonate and silica; and organic pigments such as urea-formalin resins, styrene-methacrylic acid copolymer resins and polystyrene resins.

10 [0037]

Examples of the electron beam-curable unsaturated organic compound to be used in the outer coating layer forming a part of the gloss layer of the invention include acrylate or methacrylate monomers and  
15 oligomers having at least one ethylenically unsaturated bond. It is preferred that the main component be selected from the oligomers so as to provide the desired toughness.

[0038]

Monomers having at least one ethylenically unsaturated bond for use in the invention are not limited.  
20 Examples of monofunctional monomers include N-vinylpyrrolidone, acrylonitrile or derivatives thereof, styrene or derivatives thereof, acrylamide and like amide group-containing monomers; benzyl acrylate, 2-ethylhexyl  
25 acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl

(meth)acrylate, tetrahydrofurfuryl acrylate, phenoxyethyl acrylate, nonylphenoxyethyl acrylate, acrylates of  $\epsilon$ -caprolactone adducts, butoxyethyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl acrylate, cyclohexyl

5 (meth)acrylate, N,N-dimethylamino (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, 3-phenoxypropyl acrylate, 2-methoxyethyl (meth)acrylate and like acrylates or methacrylates. Examples of monomers having two or more ethylenically unsaturated bonds include hexanediol

10 diacrylate, neopentyl glycol diacrylate, diethylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecane-dimethylol diacrylate, trimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, diacrylate of ethylene oxide-modified

15 bisphenol A and the like.

[0039]

Other examples of compounds that can serve as lubricants include stearyl-modified pentaerythritol diacrylate, lauryl (meth)acrylate and like fatty acid-

20 modified acrylates or methacrylates, silicone-modified (meth)acrylates, fluorine-modified (meth)acrylates, etc. These compounds, having at least one ethylenically unsaturated bond, can be used either singly or in a combination of two or more species as required.

25 [0040]

Examples of acrylate or methacrylate oligomers having at least one ethylenically unsaturated bond include, for example, urethane acrylate oligomers, polyester acrylate oligomers and butadiene-modified acrylate  
5 oligomers. These oligomers can be used singly or in a combination of two or more species.

[0041]

When the coating composition, which is obtained by dispersing a white pigment in the ethylenically-  
10 unsaturated-bond-containing monomer or oligomer described above, has high viscosity, it is effective that the coating composition be either diluted with an organic solvent, then applied and dried, or that it be emulsified for increased operability or diluted with water (if it is  
15 water-soluble), then applied and dried, and finally cured with an electron beam. The electron beam-curable composition according to the invention may incorporate a polymer that is soluble therein. However, the use of the polymer in an excessively large amount impairs the  
20 curability of the coating film and is not preferable from the standpoint of resistance to scratches, resistance to organic solvents, etc.

[0042]

If necessary, a non-reactive lubricant having no  
25 ethylenically unsaturated bond may also be used, insofar

as it does not impair the desired curability as in the case of other non-reactive substances. Examples of non-reactive lubricants for use in the outer coating layer forming a part of the gloss layer include zinc stearate, 5 calcium stearate, polyethylene wax, carnauba wax, paraffin wax, ester wax and like waxes, lauryl phosphate, oleyl phosphate, stearyl phosphate and like alkyl phosphates and alkali metal salts or amine salts, lauryl sulfonate, oleyl sulfonate, stearyl sulfonate and like alkyl sulfonates and 10 alkali metal salts or amine salts, glyceryl monomyristate, glyceryl monostearate, glyceryl monooleate, glyceryl distearate, glyceryl dioleate and like glyceryl fatty acid esters, diglyceryl monolaurate, diglyceryl dilaurate, tetraglyceryl monolaurate, hexaglyceryl monolaurate, 15 decaglyceryl monolaurate and like polyglyceryl fatty acid esters, dimethylpolysiloxane, and their modified products. Selection should be made from those which do not cause desensitization, decoloring or fogging.

[0043]

20           The above white pigment can be dispersed in the electron beam-curable unsaturated organic compound with the use of a three roll mill, two roll mill, Cowles Dissolver, homomixer, sand grinder, paint conditioner, ultrasonic dispersing machine or the like. The outer 25 coating layer coating composition can be applied using a

technique generally employed by those skilled in the art, such as offset gravure coating, air knife coating, Meyer bar coating, blade coating, reverse roll coating or slit die coating.

5 [0044]

The inner coating layer, which forms a part of the gloss layer of the invention, can be formed by applying a coating composition comprising as a main component an unsaturated organic compound curable by  
10 irradiation with an electron beam such that the coating amount after drying is 1.0 to 10.0 g/m<sup>2</sup>. If the coating amount is more than 10.0 g/m<sup>2</sup>, the sensitivity is deteriorated and, even with the help of an increased coating amount of the heat-sensitive coloring layer, the  
15 recording density is decreased. If the coating amount is less than 1.0 g/m<sup>2</sup>, the outer coating layer containing a large amount of white pigment cannot be satisfactorily released from the shaping surface and, further, the adhesion of the inner coating layer to the heat-sensitive  
20 coloring layer or the intermediate layer is not sufficient.

[0045]

The electron beam-curable unsaturated organic compound to be used in the inner coating layer forming a part of the gloss layer of the present invention may be  
25 suitably selected from those used for the outer coating

layer coating composition. The inner coating layer coating composition may further contain a white pigment, lubricant, etc., suitably selected from those used for the outer coating layer coating composition.

5 [0046]

The outer coating layer and the inner coating layer are brought into close contact each other to thereby form an electron beam-curable gloss layer of the invention, and then cured and unified by irradiation with an electron beam in accordance with either of the following two methods. One method comprises bringing the outer coating layer provided on the highly smooth shaping surface into close contact with the inner coating layer provided on the heat-sensitive coloring layer or the intermediate layer, and irradiating the resulting laminate with an electron beam from the opposite side of the heat-sensitive recording sheet or from the shaping surface side. The other method comprises directly applying the inner coating layer coating composition onto the outer coating layer provided on the highly smooth shaping surface, bringing the obtained layer into close contact with the heat-sensitive coloring layer or the intermediate layer, and irradiating the resulting laminate with an electron beam from the opposite side of the heat-sensitive recording sheet or from the shaping surface side. The latter method

10  
15  
20  
25



may be performed in a similar way to that of the former method if the inner coating layer coating composition is high in viscosity and therefore less likely to penetrate into the outer coating layer coating composition.

5 [0047]

The surface of the gloss layer formed as described above exhibits high smoothness, excellent glossiness and image clarity. Specifically, it is preferred that the glossiness be 80% or higher when  
10 measured at an angle of 75 degrees in accordance with JIS-Z-8714, and that the image clarity be 80% or higher, preferably 90%, when converted from the value of distinctness of image measured at an optical comb width of 2 mm in accordance with JIS-K-7105.

15 [0048]

[EXAMPLES]

The present invention will be described below in further detail with reference to the following examples to which, however, the invention is not limited. The parts  
20 and percentages used in the examples are all by weight unless otherwise specified.

Example 1

A heat-sensitive coloring layer coating composition obtained as described later was applied to one  
25 surface of commercially available synthetic paper (trade

name "YUPO FPG80", product of YUPO Corporation) in an amount of 5.5 g/m<sup>2</sup> on a dry weight basis by a bar coating method, and thereon was applied an intermediate layer coating composition in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis. To the resultant intermediate layer, an inner coating layer coating composition for gloss layer was applied in an amount of 3.0 g/m<sup>2</sup>, thereby forming an inner coating layer. Aside from the above, an outer coating layer coating composition was applied to a 75-μm-wide PET film (trade name "Lumirror T", product of TORAY Industries, Inc.) in an amount of 3.0 g/m<sup>2</sup> on a dry weight basis, thereby forming an outer coating layer. Subsequently, the outer coating layer was brought into close contact with the inner coating layer to form a gloss layer composed of the outer coating layer and the inner coating layer, which was then cured by irradiation with an electron beam from the PET film side at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV with an electron-curtain type electron beam accelerator (product of Energy Sciences, Inc.), thereby completely unifying the outer coating layer with the inner coating layer. Thereafter, the PET film was separated from the gloss layer, whereby a heat sensitive recording sheet was obtained.

• Preparation of heat-sensitive coloring layer coating composition

Dispersion A (heat-sensitive color-forming dye dispersion)

3-(N,N-dibutyl)amino-6-methyl-7-

5	anilino-fluoran	20 parts
	10% aqueous solution of polyvinyl alcohol	20 parts
	Water	10 parts

Dispersion B (developer dispersion)

	4-hydroxy-4'-isopropoxydiphenylsulfone	50 parts
10	10% aqueous solution of polyvinyl alcohol	50 parts
	Water	25 parts

[0050]

Each of Dispersions A and B were separately dispersed and pulverized to an average particle size of  
15 1.0±0.3 μm with an Ultra Visco Mill. Thereafter, 30 parts of Dispersion A, 90 parts of Dispersion B, 52 parts of a 60% slurry of calcium carbonate, 40 parts of a 10% aqueous solution of polyvinyl alcohol, 28 parts of a SBR latex (trade name "L-1537", solid conc. 50%, product of Asahi  
20 Chemical Industry Co., Ltd.), 11 parts of stearic acid amide (trade name "Cerozol A-877", solid conc. 26.5%, product of Chukyo Yushi Co., Ltd.) and 82 parts of water were mixed to thereby obtain a heat-sensitive coloring layer coating composition.

25 [0051]

- Intermediate layer coating composition (solid conc. 15%)

An intermediate layer coating composition was prepared by mixing the following:

	60% dispersion of kaolinitic clay (with an	
5	average particle size of 0.6 $\mu$ m)	72 parts
	Aqueous solution of carboxylic acid-	
	modified polyvinyl alcohol (solid conc. 10%)	
	(trade name "Gohsenal T-330", product of	
	The Nippon Synthetic Chemical Industry	
10	Co., Ltd.)	200 parts
	Acrylic emulsion	
	(trade name "SC-2250", solid conc. 40%,	
	product of Nippon Shokubai Co., Ltd.)	55 parts
	Solution of dimethylolurea	
15	(trade name "J-001", solid conc. 30%,	
	product of Showa Denko K.K.)	33 parts
	40% dispersion of zinc stearate	
	(with an average particle size of 0.9 $\mu$ m)	
	(trade name "Hymicron F-930",	
20	product of Chukyo Yushi Co., Ltd.)	13 parts
	Water	295 parts

[0052]

- Outer coating layer coating composition for gloss layer

An outer coating layer coating composition for  
25 gloss layer was prepared by mixing the following:

	Ground calcium carbonate	
	(trade name "NS-1000", product of	
	Nitto Funka Kogyo K.K.)	70 parts
	Urethane acrylate emulsion	
5	(trade name "EM90", solid conc. 40%, product	
	of Arakawa Chemical Industries, Ltd.)	65 parts
	Polysiloxane	
	(trade name "SM7025",	
	solid conc. 33%, product of	
10	Dow Corning Toray Silicone Co., Ltd.)	12 parts
	Water	40 parts

[0053]

- Inner coating layer coating composition for gloss layer

An inner coating layer coating composition for  
15 gloss layer was prepared by mixing the following:

	Urethane acrylate oligomer	
	(trade name "BS550", product of	
	Arakawa Chemical Industries, Ltd.)	70 parts
	Trimethylolpropane triacrylate	30 parts

20 In addition, before forming a gloss layer, a  
back layer coating composition was applied to the opposite  
side of the substrate in an amount of 1.5 g/m<sup>2</sup> on a dry  
weight basis by a bar coating method, after which the  
obtained coating was subjected to a smoothing treatment  
25 with a super calender.

[0054]

• Back layer coating composition

A back layer coating composition was prepared by mixing the following:

5	Sodium polystyrene sulfonate (solid conc. 33%) (trade name "CHEMISTAT SA-9", product of Sanyo Chemical Industries, Ltd.)	30 parts
	SBR latex (solid conc. 50%) (trade name "0528", product of JSR Corporation)	70 parts
10	10% aqueous solution of oxidized starch (trade name "ACE A", product of Oji Cornstarch Co., Ltd.)	150 parts
	60% slurry of kaolinitic clay	67 parts
15	Water	83 parts

[0055]

Example 2

A heat-sensitive coloring layer coating composition obtained as described in Example 1 was applied to one surface of commercially available synthetic paper (trade name "YUPO FPG80", product of YUPO Corporation) in an amount of 5.0 g/m<sup>2</sup> on a dry weight basis by a bar coating method, and thereon was applied an intermediate layer coating composition obtained as described in Example 1 in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis. To the

resultant intermediate layer, an inner coating layer coating composition for gloss layer obtained as described later was applied in an amount of  $3.5 \text{ g/m}^2$ , thereby forming an inner coating layer. Aside from the above, an  
5 outer coating layer coating composition was applied to a chromium-plated highly smooth metal plate in an amount of  $3.0 \text{ g/m}^2$  on a dry weight basis, thereby forming an outer coating layer. Subsequently, the outer coating layer was brought into close contact with the inner coating layer to  
10 form a gloss layer composed of the outer coating layer and the inner coating layer, which was then cured by irradiation with an electron beam from the back layer side at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV with an electron-curtain type electron  
15 beam accelerator (product of Energy Sciences, Inc.), thereby completely unifying the outer coating layer with the inner coating layer. After the curing was completed, the metal plate was separated from the gloss layer, whereby a heat sensitive recording sheet was obtained. As  
20 in Example 1, before forming the gloss layer, a back layer coating composition was applied to the opposite side of the substrate in an amount of  $1.5 \text{ g/m}^2$  on a dry weight basis by a bar coating method, after which the obtained coating was subjected to a smoothing treatment with a  
25 super calender.

[0056]

- Outer coating layer coating composition for gloss layer

An outer coating layer coating composition for gloss layer was prepared by mixing the following:

5	Precipitated calcium carbonate (trade name "Brilliant-15", product of Shiraishi Kogyo Kaisha, Ltd.)	30 parts
	No. 1 fraction kaolin (trade name "UW-90", product of Engelhard Corporation)	40 parts
10	Urethane acrylate emulsion (trade name "NR440", solid conc. 40%, product of Zenica)	65 parts
	Polysiloxane (trade name "SM7025", solid conc. 33%, product of Dow Corning Toray Silicone Co., Ltd.)	12 parts
15	Water	45 parts

[0057]

- Inner coating layer coating composition for gloss layer

20 An inner coating layer coating composition for gloss layer was prepared by mixing the following:

	Urethane acrylate oligomer (trade name "BS551", product of Arakawa Chemical Industries, Ltd.)	70 parts
25	tripropylene glycol diacrylate	30 parts



[0058]

Example 3

A heat-sensitive coloring layer coating composition obtained as described in Example 1 was applied to one surface of commercially available synthetic paper (trade name "YUPO FPG80", product of YUPO Corporation) in an amount of 5.0 g/m<sup>2</sup> on a dry weight basis by a bar coating method, and thereon was applied an intermediate layer coating composition obtained as described in Example 1 in an amount of 2.0 g/m<sup>2</sup> on a dry weight basis. To the resultant intermediate layer, an inner coating layer coating composition for gloss layer was applied in an amount of 4.0 g/m<sup>2</sup>, thereby forming an inner coating layer. Aside from the above, an outer coating layer coating composition was applied to a 75-μm-wide PET film (trade name "Lumirror T", product of TORAY Industries, Inc.) in an amount of 3.0 g/m<sup>2</sup> on a dry weight basis, thereby forming an outer coating layer. Subsequently, the outer coating layer was brought into close contact with the inner coating layer to form a gloss layer composed of the outer coating layer and the inner coating layer, which was then cured by irradiation with an electron beam from the PET film side at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV with an electron-curtain type electron beam accelerator (product of Energy Sciences,

Inc.), thereby completely unifying the outer coating layer with the inner coating layer. After the curing was completed, the PET film was separated from the gloss layer, whereby a heat sensitive recording sheet was obtained. As  
5 in Example 1, before forming the gloss layer, a back layer coating composition was applied to the opposite side of the substrate in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis by a bar coating method, after which the obtained coating was subjected to a smoothing treatment with a  
10 super calender.

[0059]

- Outer coating layer coating composition for gloss layer

An outer coating layer coating composition for gloss layer was prepared by mixing the following:

15	Calcium carbonate (trade name "Raiton A", product of Bihokufunka Kogyo K.K.)	62 parts
	Urethane acrylate oligomer (trade name "EB294", product of Daicel-UCB Co., Ltd.)	35 parts
20	Polysiloxane (trade name "PERENOL S43", solid conc. 30%, product of San Nopco Limited)	10 parts
	Toluene	40 parts

25 [0060]

- Inner coating layer coating composition for gloss layer

An inner coating layer coating composition for gloss layer was prepared by mixing the following:

Urethane acrylate oligomer

- |   |                                    |          |
|---|------------------------------------|----------|
| 5 | (trade name "BS551", product of    |          |
|   | Arakawa Chemical Industries, Ltd.) | 70 parts |
|   | tripropylene glycol diacrylate     | 30 parts |

[0061]

Comparative Example 1

- 10           A heat-sensitive recording sheet was obtained in the same manner as in Example 1 except that the outer coating layer coating composition for gloss layer was replaced with the one prepared by mixing the following:

Ground calcium carbonate

- |    |                                   |          |
|----|-----------------------------------|----------|
| 15 | (trade name "NS-1000", product of |          |
|    | Nitto Funka Kogyo K.K.)           | 22 parts |

Urethane acrylate emulsion

- |  |  |           |
|--|--|-----------|
|  | (trade name "EM90", solid conc. 40%, product |           |
|  | of Arakawa Chemical Industries, Ltd.)        | 185 parts |

- 20           Polysiloxane

- |  |                                       |          |
|--|---------------------------------------|----------|
|  | (trade name "SM7025",                 |          |
|  | solid conc. 33%, product of           |          |
|  | Dow Corning Toray Silicone Co., Ltd.) | 12 parts |

[0062]

- 25           Comparative Example 2

A heat-sensitive coloring layer coating composition obtained as described in Example 1 was applied to one surface of commercially available synthetic paper (trade name "YUPO FPG80", product of YUPO Corporation) in an amount of 5.5 g/m<sup>2</sup> on a dry weight basis by a bar coating method, and thereon was applied an intermediate layer coating composition obtained as described in Example 1 in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis. Aside from the above, a gloss layer coating composition was applied to a 75- $\mu$ m-wide PET film (trade name "Lumirror T", product of TORAY Industries, Inc.) in an amount of 3.0 g/m<sup>2</sup>. Subsequently, the coated surface of the formed gloss layer was brought into close contact with the intermediate layer, and the gloss layer was then cured by irradiation with an electron beam from the PET film side at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV with an electron-curtain type electron beam accelerator (product of Energy Sciences, Inc.). After the curing was completed, the PET film was separated from the gloss layer, whereby a heat sensitive recording sheet was obtained. As in Example 1, before forming the gloss layer, a back layer coating composition was applied to the opposite side of the substrate in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis by a bar coating method, after which the obtained coating was subjected to a smoothing

treatment with a super calender.

[0063]

• Gloss layer coating composition

A gloss layer coating composition was obtained  
5 by mixing the following:

	Urethane acrylate oligomer	
	(trade name "EB284",	
	product of Daicel-UCB Co., Ltd.)	55 parts
	Trimethylolpropane triacrylate	35 parts
10	Silicone acrylate	
	(trade name "EB350",	
	product of Daicel-UCB Co., Ltd.	7 parts
	Polysiloxane	
	(trade name "PERENOL S43", solid conc. 30%,	
15	product of San Nopco Limited)	10 parts

[0064]

Comparative Example 3

A heat-sensitive coloring layer coating  
composition obtained as described in Example 1 was applied  
20 to one surface of commercially available synthetic paper  
(trade name "YUPO FPG80", product of YUPO Corporation) in  
an amount of 5.0 g/m<sup>2</sup> on a dry weight basis by a bar  
coating method, and thereon was applied an intermediate  
layer coating composition obtained as described in Example  
25 1 in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis. To the

resultant intermediate layer, a gloss layer coating composition was applied in an amount of 3.5 g/m<sup>2</sup>. The formed gloss layer was then cured by irradiation with an electron beam from the gloss layer coating composition side at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV with an electron-curtain type electron beam accelerator (product of Energy Sciences, Inc.), whereby a heat sensitive recording sheet was obtained. As in Example 1, before forming the gloss layer, a back layer coating composition was applied to the opposite side of the substrate in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis by a bar coating method, after which the obtained coating was subjected to a smoothing treatment with a super calender.

15 [0065]

• Gloss layer coating composition

A gloss layer coating composition was obtained by mixing the following:

20	Urethane acrylate oligomer (trade name "EB284", product of Daicel-UCB Co., Ltd.)	65 parts
	Trimethylolpropane triacrylate	25 parts
	Silicone acrylate (trade name "EB350", product of Daicel-UCB Co., Ltd.)	7 parts

Polysiloxane

(trade name "PERENOL S43", solid conc. 30%,

product of San Nopco Limited)

10 parts

[0066]

5           Each of the heat-sensitive recording sheets  
obtained in Examples 1 to 3 and Comparative Examples 1 to  
3, having a width of 110 nm [sic], was subjected to a  
recording operation using a thermal printer (available  
under the trade name of "UP-860", from Sony Corporation).

10   Image quality, recording problems and improper advance of  
the recording sheet were checked and rated on the  
following criteria.

(1) Glossiness

          The glossiness was measured for five times in  
15   accordance with the procedure of JIS-Z-8741 (specular  
gloss at an incident angle of 75 degrees and an acceptance  
angle of 75 degrees) using a glossmeter (available under  
the trade name of "VG-10", from Nippon Denshoku Industries,  
Co., Ltd.), and the results were averaged.

20   (2) Image clarity

          The image clarity was expressed in terms of the  
value of distinctness of image measured at an optical comb  
width of 2 mm in accordance with JIS-K-7105.

[0067]

25   (3) Image quality

Each of the five recorded heat-sensitive recording sheets were visually inspected for distinctness, contrast and density irregularity in the image, and rated on the following criteria. : Good; ~Δ: Fairly good; Δ:

5 Neither good nor bad, Δ~x; Fairly bad; x: Bad.

(4) Recording problems

Each of the five recorded heat-sensitive recording sheets were visually inspected in terms of recording problems resulting from the running trace of the thermal recording head or the grinding debris adhered to the same, and rated on the following criteria. : Good; ~Δ: Fairly good; Δ: Neither good nor bad, Δ~x; Fairly bad; x: Bad.

(5) Improper advance of the recording sheet

15 Each of the five recorded heat-sensitive recording sheets were visually inspected in terms of duration of operation and recording irregularities with horizontal stripes, and rated on the following criteria. : Good; ~Δ: Fairly good; Δ: Neither good nor  
20 bad, Δ~x; Fairly bad; x: Bad.

[0068]

As is evident from the results shown in Table 1, the heat-sensitive recording sheets of Examples 1 to 3 provided recorded images that were superior in image  
25 quality, glossiness and image clarity, as well as



providing excellent recording characteristics, whereas the heat-sensitive recording sheets of Comparative Examples 1 to 3 showed in some respects lower performance than those of Examples 1 to 3, the degrees of which varied depending on the sheet.

[0069]

[Table 1]

No.	Glossi- ness	Image clarity	Image quality	Recording problems	Improper advance of the recording sheet
Ex. 1	91	95	o	o	o
Ex. 2	92	94	o	o	o
Ex. 3	92	95	o	o	o
Comp. Ex. 1	92	95	o	o~Δ	Δ
Comp. Ex. 2	93	95	o	Δ	Δ
Comp. Ex. 3	85	81	Δ	Δ~x	Δ~x

10 [0070]

[Effects of the Invention]

As is apparent from Table 1 above, the heat-sensitive recording sheet of the present invention provides recorded images that are excellent in image quality, glossiness and image clarity, as well as

15

excellent recording characteristics, and thus is very useful in practical applications.

[Brief Description of the Drawings]

[Fig. 1]

5           A schematic drawing illustrating a process in which a metal cylindrical rotator is used to form a gloss layer composed of two layers of the heat-sensitive recording sheet of the present invention.

[Fig. 2]

10           A schematic drawing illustrating a process in which a sheet material is used to form a gloss layer composed of two layers of the heat-sensitive recording sheet of the present invention.

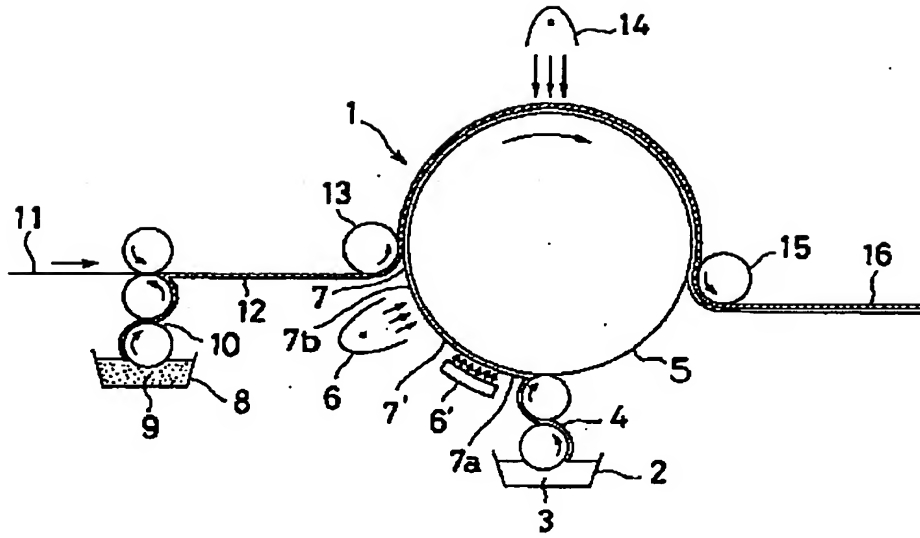
[Explanation of Numerals]

- 15   1.   Curing facility  
     2.   Coating composition container  
     3.   Second coating composition  
     4.   Second coater  
     5.   Metal cylindrical rotator  
20   6.   First electron beam irradiator  
     6'.   Dryer which uses infrared rays and/or hot air  
     7a.   Second coating layer  
     7'.   Dried second coating layer  
     7b.   Cured second coating layer  
25   7.   Second coating layer

- 9. First coating composition
- 10. First coater
- 11. Sheet substrate
- 12. First coating layer
- 5 13. Guide roll
- 14. Second electron beam irradiator
- 15. Releasing roll
- 16. Heat-sensitive recording sheet
- 17. Sheet material

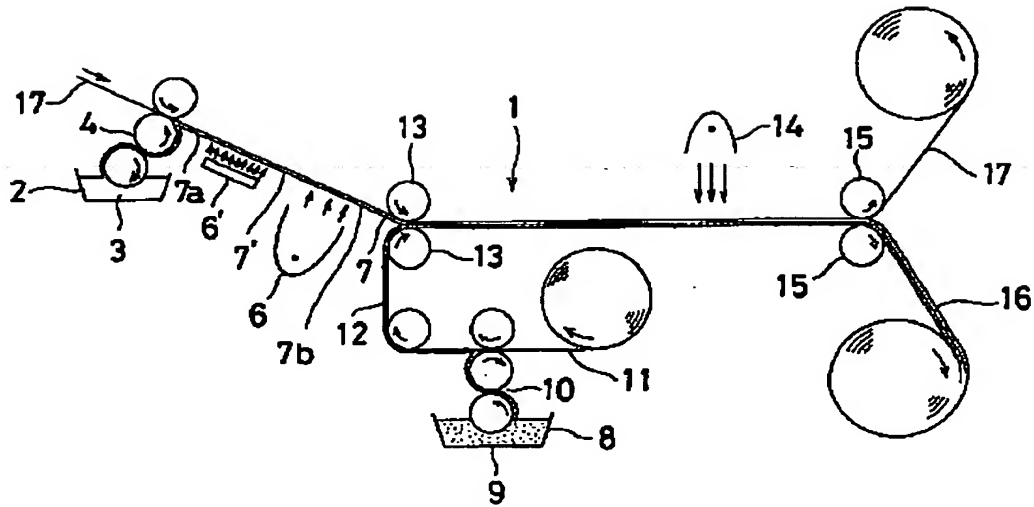
10

[Fig. 1]



5

[Fig. 2]



5

10

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(54) 【発明の名称】 感熱記録体

(57) 【要約】

【目的】 画質が良好で高い光沢と写像性を有すことに加えて優れたプリント特性を有する感熱記録体を提供する。

【構成】 基材の少なくとも片面上に感熱発色層を設け、該感熱発色層上又は該感熱発色層上に必要に応じて中間層を設けた後、該感熱発色層又は該中間層上に形成する光沢層が白色顔料と電子線照射により硬化し得る不飽和有機化合物を含有する外側塗工層と、電子線照射により硬化し得る不飽和有機化合物を主成分とする内側塗工層から成り、かつ外側塗工層は高平滑性を有する成形面から剥離して得られた感熱記録体において、該内側塗工層の塗膜のヤング率が20℃の温度において、50 Kg/mm<sup>2</sup>以上である感熱記録体。

【効果】 画質が良好で高い光沢と写像性を有すことに加えて優れたプリント特性を有する。

## 【特許請求の範囲】

【請求項1】 基材の少なくとも片面上に感熱発色層を設け、該感熱発色層上に必要に応じて中間層を設けた後、該感熱発色層又は該中間層上に形成する光沢層が白色顔料と電子線照射により硬化し得る不飽和有機化合物を含有する外側塗工層と、電子線照射により硬化し得る不飽和有機化合物を主成分とする内側塗工層からなり、かつ外側塗工層は高平滑性を有する成型面から剥離して得られた感熱記録体において、該内側塗工層の塗膜のヤング率が20℃の温度において、50Kg/mm<sup>2</sup>以上であることを特徴とする感熱記録体。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は感熱記録体に関するものである。さらに詳しくは、本発明は、画質が良好で、高い光沢、写像性を有する記録画像が得られることに加えて優れたプリント特性を有するものである。

## 【0002】

【従来の技術】 感熱記録体は、一般に紙、合成紙、またはプラスチックフィルム等からなる支持体の片面上に、電子供与性ロイコ染料のような無色または淡色の発色性物質と、電子受容性のフェノール化合物のような有機酸性顔色剤と、接着剤とを主成分として含む感熱発色層を設けたものであって、これら発色性染料と顔色剤とを熱エネルギーによって反応させて発色記録画像をえることができる。このような感熱記録体は、記録装置がコンパクトでしかも安価であり、かつ保守が容易であることなどの利点を有し、ファクシミリや自動券売機、科学計測機の記録用媒体としてだけでなく、POSラベル、CAD、CRT医療画像用等の各種プリンター、プロッターの出力媒体として広く使用されている。

【0003】 その中で記録画像の均一性、高解像度が必要なCRT医療計測用の画像プリンター及び、寸法安定性、細線記録の必要なCADプロッターには複層構造を有する合成紙や、必要に応じて無機顔料を含有する2軸延伸した熱可塑性樹脂フィルムが使用されている。一方、ビデオプリンター用紙等の高付加価値感熱記録体には高画質に加え、高い光沢、写像性を有することが要望されている。ただし、記録画像の均一性、解像度といった画質に加え、高い光沢、写像性を有するためには、基材の地合、クッション性等に加えて感熱記録体最表面層を高平滑にする必要がある。

【0004】 感熱記録体の最表面層を高平滑にするには、例えば、特開昭62-279980号公報に提案されているような紫外線、電子線により硬化する塗料を使用する方法がある。しかし、この方法では、硬化時の収縮により表面にさざ波状模様が生じるため、高い光沢は得られても高い写像性を得ることができず、品質的に不十分であった。本発明者らは、このような問題について鋭意検討を重ねた結果、感熱記録体に光沢層を設ける場

合、電子線照射により硬化し得る不飽和有機化合物を主成分とする塗料を、基材感熱発色層上もしくは中間層を感熱発色層上に設けた場合は中間層上に塗工し、高い平滑表面を有する成型面と圧着させた後、電子線により硬化させるか、あるいは該成型面上に該塗料を塗工し、基材感熱発色層もしくは中間層を感熱発色層上に設けた場合は中間層と貼り合わせた後、電子線により硬化させ、その後該成型面を剥離させることで、該成型面の有する高い平滑性を電子線により硬化された光沢層表面に転写させ、硬化収縮に伴うさざ波状模様が全くなく高い光沢と写像性を付与することができることを見だし、さきに特願平5-202039号明細書として出願した。

【0005】 ところが、感熱記録体最表面層を高平滑にすると、最表面層と感熱記録ヘッドとの接触面積が増えることにより、感熱記録ヘッドの走行跡あるいは感熱記録ヘッドが最表面層を削りその削り粕が感熱記録ヘッドに付着することによって生じる印字障害が顕著になることに加えて、高温時に感熱記録ヘッドと最表面層が粘着しやすくなることにより走行不良が生じる等、高平滑にすることに対する技術的課題が指摘された。

【0006】 そのため、本発明者らはその解決方法として、光沢層が白色顔料と電子線照射により硬化し得る不飽和有機化合物を特定量配合する外側塗工層と電子線照射により硬化し得る不飽和有機化合物を主成分とする内側塗工層からなり、かつ外側塗工層は高平滑を有する成型面から剥離する方法を見出し、さきに特願平5-291552号明細書として出願した。しかし、上記の如く、外側塗工層中に白色顔料と電子線照射により硬化し得る不飽和有機化合物を特定量配合することにより、硬化塗膜の硬度と強靱性を向上させることによって、印字障害、走行不良等が未だ不十分であり改善が必要であった。

## 【0007】

【発明が解決しようとする課題】 本発明は従来の感熱記録体の有する上記問題点を解消し、高い光沢、写像性を有することに加え、画質が良好で優れたプリント特性を有する感熱記録体を提供するものである。

## 【0008】

【課題を解決するための手段】 本発明者らは、前記目的を達成するために鋭意検討を重ねた結果、電子線照射により硬化し得る不飽和有機化合物を主成分とする内側塗工層の塗膜物性、特に塗膜のヤング率が特定の領域以上であるとき、画質が良好で高い光沢、写像性を有することに加え、優れたプリント特性を有する感熱記録体が見出され、本発明を完成するに至った。

【0009】 すなわち本発明は、基材の少なくとも片面上に感熱発色層を設け、該感熱発色層上に必要に応じて中間層を設けた後、該感熱発色層又は該中間層上に形成する光沢層が白色顔料と電子線照射により硬化し得る不飽和有機化合物を含有する外側塗工層と、電子線照射に

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より硬化し得る不飽和有機化合物を主成分とする内側塗工層からなり、かつ外側塗工層は高平滑性を有する成型面から剥離して得られた感熱記録体において、該内側塗工層の塗膜のヤング率が20℃の温度において、50Kg/mm<sup>2</sup>以上であることを特徴とする感熱記録体である。

【0010】本発明で使用する基材は、ポリオレフィン系樹脂と白色無機顔料を加熱混練し、ダイから押し出し、縦方向に延伸したものの両面にポリオレフィン系樹脂と白色無機顔料からなるフィルムを片面当たり1~2層積層し、横方向に延伸して半透明化あるいは不透明化して製造される合成紙、及びポリエチレン、ポリプロピレン、エチレン-酢酸ビニル共重合樹脂、ポリ塩化ビニル、ポリスチレン、ポリエステル等の熱可塑性樹脂単独又は混合物を加熱混練し、ダイから押し出し2軸延伸して得られたフィルムや、これらの樹脂に白色無機顔料を混合し、2軸延伸した不透明フィルムのほか、上質紙、中質紙、ロール紙、再生紙、塗工紙等のパルプ繊維から製造されたものが使用できる。パルプ繊維からなる支持体は画像の均一性を良くするため、あらかじめ塗工層を設けた後、感熱層を塗工することが望ましい。

【0011】本発明の感熱発色層は、無色又は淡色の電子供与性ロイコ染料、加熱により該ロイコ染料を発色させる有機酸性物質および接着剤を主成分として含有するほか、必要に応じて架橋剤、顔料、熱可塑性物質を添加した感熱発色層塗料を塗工することにより設けることができる。感熱発色層の塗工量は、発色感度、発色濃度の点で一般に3~15g/m<sup>2</sup>が好ましい。塗工方法はエアナイフ方式、メイヤーバー方式、ブレード方式、リバーシロール方式、スリットダイ方式等の従来から当業者で使用されている方式を利用することができる。また感熱発色層の表面をスーパーカレンダー、グロスカレンダー、マシンカレンダー等により平滑化処理を行うことにより塗工性を高め、記録濃度、感度を向上させることができる。

【0012】発色性染料としては、顕色剤と加熱下に反応して発色することができる無色又は淡色の電子供与性ロイコ染料が用いられる。本発明に用いられる発色性染料は、例えば、2,2ビス〔4-〔6'-（N-シクロヘキシル-N-メチルアミノ）-3'-メチルスピロ（フタリド-3,9'-キサンテン）-2'-イルアミド〕フェニル〕プロパン、3-ジエチルアミノ-6メチル-7-アニリノフルオラン、3-ビペリジノ-6-メチル-7-アニリノフルオラン、3-（N-メチル-N-シクロヘキシル）アミノ-6-メチル-7-アニリノフルオラン、3-ジメチルアミノ-7-クロロアニリノフルオラン、3-〔N-エチル-N-（p-メチルフェニル）アミノ〕-6-メチル-7-アニリノフルオラン、3-ジエチルアミノ-7-（メタトリフルオロメチル）アニリノフルオラン、3-（N-エチル-N-テト

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ラヒドロフルリル）アミノ-6-メチル-7-アニリノフルオラン、3-（N-エチル-N-イソペンチル）アミノ-6-メチル-7-アニリノフルオラン、3-（N,Nジブチル）アミノ-6-メチル-7-アニリノフルオラン等のフルオラン系染料の少なくとも1員からなるものである。

【0013】本発明に用いられる顕色剤は、発色性染料と加熱下に反応してこれを発色させることのできる電子受容性有機酸性物質からなるものである。このような顕色剤は、常温以上、好ましくは70℃以上で液化または気化して、上記発色性染料と反応してこれらが発色させるものである。顕色剤は発色濃度を最高とするため、通常、発色性染料1重量部に対し1~5重量部、好ましくは1.5~3重量部の割合で混合使用される。

【0014】顕色剤は、例えば、4,4'-イソプロピリデンジフェノール（ビスフェノールA）、4,4'-イソプロピリデンビス（2-クロロフェノール）、4,4'-イソプロピリデンビス（2-メチルフェノール）、4,4'-イソプロピリデンビス（2,6-tert-ブチルフェノール）、4,4'-sec-ブチリデンジフェノール、4,4'-シクロヘキシリデンジフェノール、4-tert-ブチルフェノール、4-フェニルフェノール、4-ヒドロキシジフェノキシド、4,4'-ジヒドロキシジフェニルスルホン、2,4'-ジヒドロキシジフェニルスルホン、3,3'-ジヒドロキシジフェニルスルホン、3,3'-ジアミノ-4,4'-ジヒドロキシジフェニルスルホン、3,3'-ジアリル-4,4'-ジヒドロキシジフェニルスルホン、3,3'-ジクロロ-4,4'-ジヒドロキシジフェニルスルホン、4-ヒドロキシ-4'-イソプロピルオキシジフェニルスルホン、4-ヒドロキシ-4'-ベンジルオキシジフェニルスルホン、2,4-ジヒドロキシジフェニルスルホン、2,4-ジヒドロキシ-4'-メチルジフェニルスルホン、および3,4-ジヒドロキシフェニル-p-トリルスルホンなどから選ばれた少なくとも1員からなるものである。

【0015】本発明において、感熱発色層に含まれる接着剤は水溶性樹脂及び水分散性樹脂のいずれも使用可能である。例えば、ポリビニルアルコール、澱粉、変性澱粉、アラビアゴム、ゼラチン、カゼイン、キトサン、メチルセルロース、ヒドロキシメチルセルロース、ヒドロキシエチルセルロース、ポリビニルピロリドン、ポリアクリル酸塩、ポリアクリルアミド、ポリエステル樹脂、スチレン-アクリル酸エステル共重合樹脂、スチレン-無水マレイン酸共重合樹脂、メチルビニルエーテル-無水マレイン酸共重合樹脂、イソプロピレン-無水マレイン酸共重合樹脂等の水溶性樹脂、および、酢酸ビニルエマルジョン、アクリル酸エステル共重合エマルジョン、メタクリル酸エステル共重合エマルジョン、ポリウレタンエマルジョン、ポリ塩化ビニルエマルジョン、S



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BRラテックス、MBRラテックス等の乳化物で最低造膜温度が20℃以下の造膜性の良好な水分散性樹脂を単独又は混合して使用することができる。

【0016】しかし、前記発色性染料および顔色剤の各分散液と混合したときに混合液が発色したり、凝集したり、あるいは高粘度になったりしないことが必要であり、また形成された感熱記録層皮膜が強靱であること、減感作用がないことが必要である。感熱発色層中の接着剤の配合量は感熱発色層の固形分に対し8~20%が望ましく、8%未満では塗膜強度が低い欠点があるし、20%を越すと感度が低下する問題がある。

【0017】また感熱発色層の耐水性を向上させるためには、樹脂を硬化させるための架橋剤を使用することができる。例えば、グリオキザール、ジアルデヒド澱粉等のジアルデヒド系化合物、ポリエチレンイミン等のポリアミン系化合物、エポキシ系化合物、ポリアミド樹脂、メラミン樹脂、グリセリングリシジルエーテル等のグリシジル系化合物、ジメチロールウレア化合物、アジリジン化合物、ブロックイソシアネート化合物、並びに過硫酸アンモニウムや塩化第二鉄、および塩化マグネシウム、四ホウ酸ソーダ、四ホウ酸カリウム等の無機化合物又はホウ酸、ホウ酸トリエステル、ホウ素系ポリマーを感熱発色層の固形分に対し1~10%の範囲で用いることができる。

【0018】顔料は、感熱発色層の白色度向上、画像の均一性向上のため、白色度が高く、平均粒径が5μm以下の微粒子顔料を使用することができる。例えば、炭酸カルシウム、炭酸マグネシウム、カオリン、クレイ、タルク、焼成クレイ、シリカ、ケイソウ土、合成ケイ酸アルミニウム、酸化亜鉛、酸化チタン、水酸化アルミニウム、硫酸バリウム、表面処理された炭酸カルシウムやシリカなどの無機顔料、並びに、尿素-ホルマリン樹脂、スチレン-メタクリル酸共重合樹脂、ポリスチレン樹脂等の有機顔料が使用できる。顔料の配合量は、発色濃度を低下させないため、感熱発色層の固形分に対して40%以下が望ましい。

【0019】熱可塑性物質としては、例えば、ステアリン酸アミド、ステアリン酸ビスアミド、オレイン酸アミド、パルミチン酸アミド、ヤシ脂肪酸アミド、ベヘニン酸アミド等の脂肪酸アミド類、ステアリン酸亜鉛、ステアリン酸カルシウム、ポリエチレンワックス、カルナバロウ、パラフィンワックス、エステルワックス等のワックス類（または滑剤）、テレフタル酸ジメチルエステル、テレフタル酸ジブチルエステル、テレフタル酸ジベンジルエステル、イソフタル酸ジブチルエステル、1-ヒドロキシナフトエ酸フェニルエステル、1,2-ジ(3-メチルフェノキシ)エタン、1,2-ジフェノキシエタン、1-フェノキシ-2-(4-メチルフェノキシ)エタン、炭酸ジフェニル、p-ベンジルピフェニル、2,2'-メチレンビス(4-メチル-6-tert-

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ブチルフェノール)、4,4'-ブチリデンビス(6-tert-ブチル-3-メチルフェノール)、1,1,3-トリス(2-メチル-4-ヒドロキシ-5-tert-ブチルフェニル)ブタン、2,2'-メチレンビス(4-エチル-6-tert-ブチルフェノール)、2,4-ジ-tert-ブチル-3-メチルフェノール、4,4'-チオビス(3-メチル-6-tert-ブチルフェノール)等のヒンダードフェノール類、2-(2'-ヒドロキシ-5'-メチルフェニル)-ベンゾトリアゾール、および2-ヒドロキシ-4-ベンジルオキシベンゾフェノン等の増感剤、酸化防止剤、紫外線吸収剤等がある。

【0020】熱可塑性物質は、一般に顔色剤1重量部に対して4重量部以下の割合で感熱発色層にふくまれていることが好ましい。更に、感熱発色層塗料のヌレを良くしハジキをなくすため、アセチレングリコール、ジアルキルスルホコハク酸塩等のヌレ性向上剤や顔料の分散剤、消泡剤、蛍光染料、着色顔料等を添加することができる。

【0021】本発明の感熱記録体には光沢層と感熱発色層との密着性、光沢層塗工、硬化時の地発色防止等の点から感熱発色層と光沢層の間に中間層を設けることは有効である。この場合、感熱発色層上に水溶性及び/又は水分散性樹脂、顔料、滑剤及び架橋剤を主成分として含有する塗料を乾燥後の塗工量が1.0~5.0g/m<sup>2</sup>となるように塗工して得ることができる。塗工量が1.0g/m<sup>2</sup>未満であれば塗膜が均一に形成されないため、ピンホールや塗工欠陥が存在し、画質、表面性を低下させる原因となる。塗工量が5.0g/m<sup>2</sup>を越すと感度が低下し、印字濃度が薄くなる欠点がある。塗工方式は感熱発色層の塗工に利用した方法と同様な方法が利用できる。

【0022】また中間層の表面をスーパーカレンダー、グロスカレンダー、マシンカレンダー等により平滑化処理を行うことにより、光沢層の塗工性を高め、記録濃度、感度、光沢を向上させることができる。中間層の樹脂は、中間層固形分に対し20~80%、顔料は20~80%の範囲が良好であり、樹脂の配合比が80%を越すと記録時にスティックが発生する問題がある。また、樹脂の配合比が20%未満では、塗膜のバリエーション性が低く地発色が起きる塗料では、塗料の浸透防止能力が不足し、また感熱発色層と光沢層の密着性の改善効果も減少する。

【0023】本発明の光沢層を形成する内側塗工層としては、電子線照射により硬化する不飽和有機化合物を主成分として含有する塗料であり、塗膜物性のヤング率が20℃の温度において、50Kg/mm<sup>2</sup>以上のものが望ましく、乾燥後の塗工量が1.0~10.0g/m<sup>2</sup>となるように塗工して得ることができる。ヤング率が50Kg/mm<sup>2</sup>以上であるとき、走行不良等が改善する原因については明確ではないが、感熱記録ヘッドによる

光沢層の変形が減少するためと考えられる。塗工量が10.0 g/m<sup>2</sup>を越すと感度が低下し、感熱発色層の塗工量を増やすことで対処しても、印字濃度が低くなる欠点がある。塗工量が1.0 g/m<sup>2</sup>未満では、内側塗工層塗料に要求される白色顔料を高配合した外側塗工層の成型面からの剥離、及び感熱発色層または中間層との接着を十分に達成することが難しい。

【0024】本発明の光沢層を形成する内側塗工層塗料層に使用される電子線照射により硬化する不飽和有機化合物としては、20℃の温度において50 Kg/mm<sup>2</sup> 10以上のヤング率を持つ樹脂であれば特に制限はないが、例えば、N-ビニルピロリドン、アクリロニトリルあるいはその誘導体、スチレンあるいはその誘導体、アクリルアミド等のアミド基含有モノマー、ベンジルアクリレート、2-エチルヘキシルアクリレート、2-ヒドロキシエチル(メタ)アクリレート、2-ヒドロキシプロピル(メタ)アクリレート、テトラヒドロフルフリルアクリレート、フェノキシエチルアクリレート、ノニルフェノキシエチルアクリレート、ε-カプロラクトン付加物のアクリレート、ブトキシエチル(メタ)アクリレート 20、2-ヒドロキシ-3-フェノキシプロピルアクリレート、シクロヘキシル(メタ)アクリレート、N,N-ジメチルアミノ(メタ)アクリレート、N,N-ジメチルアミノエチル(メタ)アクリレート、3-フェノキシプロピルアクリレート、2-メトキシエチル(メタ)アクリレート、ポリオキシエチレンエピクロロヒドリン変性ビスフェノールAジアクリレート、ジシクロヘキシルアクリレート、エピクロロヒドリン変性ポリエチレングリコールジアクリレート、1,6-ヘキサジオールジアクリレート、ヒドロキシビバリン酸エステルネオペンチルグリコールジアクリレート、ノニルフェノキシポリエチレングリコールアクリレート、エチレンオキサイド変性フェノキシ化リン酸アクリレート、ポリブタジエンアクリレート、カプロラクトン変性テトラヒドロフルフリルアクリレート、トリス(アクリロキシエチル)イソシアネート、トリメチロールプロパントリアクリレート、ペンタエリスリトールトリアクリレート、ペンタエリスリトールテトラアクリレート、ジペンタエリスリールヘキサアクリレート、ポリエチレングリコールジアクリレート、1,4-ブタジエンジオールジアクリレート 40、ネオペンチルグリコールジアクリレート、及びネオペンチルグリコール変性トリメチロールプロパンジアクリレート等を1種又は2種以上を混合して使用することができる。

【0025】その中でも高架橋性を与える3官能以上の樹脂でカプロラクトン変性ジペンタエリスリトールヘキサ(ペンタ)アクリレート、エチレンオキサイド変性トリメチロールプロパントリアクリレート、ジペンタエリスリトールヘキサ(ペンタ)アクリレート等を配合比が20%以上で混合することが望ましい。配合比が20%

未満では、ヤング率が50 Kg/mm<sup>2</sup>より小さくなり、走行不良等の改善効果が得られない。

【0026】本発明の光沢層を形成する内側塗工層塗料に配合される白色顔料は、光沢層の硬度、白色度向上、印字障害、走行不良減少のため、白色度が高く、平均粒径が5 μm以下の微粒子顔料を使用することができる。例えば、炭酸カルシウム、炭酸マグネシウム、カオリン、クレー、タルク、焼成クレー、シリカ、ケイソウ土、合成ケイ酸アルミニウム、酸化亜鉛、酸化チタン、水酸化アルミニウム、硫酸バリウム、表面処理された炭酸カルシウムやシリカなどの無機顔料、並びに、尿素-ホルマリン樹脂、スチレン-メタクリル酸共重合樹脂、ポリスチレン樹脂等の有機顔料が使用できる。

【0027】前記白色顔料を電子線照射により硬化する不飽和有機化合物に分散するには、スリーロールミル、ツーロールミル、カウレスディゾルバー、ホモミキサー、サンドグラインダー、ペイントコンディショナー及び超音波分散機等を使用することができる。また内側塗工層塗料の塗工方法はオフセットグラビア方式、エアナイフ方式、メイヤーバー方式、ブレード方式、リバースロール方式、スリットダイ方式等の従来から当業者で使用されている方式を利用することができる。本発明の光沢層を形成する外側塗工層としては、白色顔料(A)と電子線照射により硬化し得る不飽和有機化合物(B)とをA/Bの重量比で40/60~95/5の割合で主成分として含有する塗料を乾燥後の塗工量が1.0~10.0 g/m<sup>2</sup>となるように塗工して得ることができる。塗工量が10.0 g/m<sup>2</sup>を越すと感度が低下し、感熱発色層の塗工量を増やすことで対処しても、印字濃度が低くなる欠点がある。塗工量が1.0 g/m<sup>2</sup>未満では、硬化後成型面からの剥離性が劣ることに加え、高い写像性、光沢度を得ることが難しい。

【0028】白色顔料の配合量は、硬化塗膜の硬度を上げる点からできるだけ多い方が好ましいが、成型面からの良好な剥離性、硬化塗膜の高い表面性を得るために、A/Bの重量比で95/5以下が好ましい。また所望の硬度を得るためにはA/Bの重量比で40/60以上が望ましい。

【0029】本発明の光沢層を形成する外側塗工層塗料に配合される白色顔料は、内側塗工層塗料に使用したものの中から適宜選択して使用することができる。本発明の光沢層を形成する外側塗工層塗料に配合される電子線によって硬化する不飽和有機化合物としては、エチレン性不飽和結合を1つ以上有するアクリレートあるいはメタクリレート系モノマーあるいはオリゴマー等を1種又は2種以上を混合して使用することができ、必要な強靱性を得るためにはオリゴマーを主成分とする配合が望ましい。

【0030】エチレン性不飽和結合を1つ以上有するアクリレートあるいはメタクリレートオリゴマーとして

は、例えばウレタンアクリレートオリゴマー、ポリエステルアクリレートオリゴマー、ブタジエン変性アクリレートオリゴマー等を1種または2種以上を混合して使用してよい。以上のエチレン性不飽和結合を有するモノマー、オリゴマーに白色顔料を分散させた塗料の粘度が高い場合は、有機溶剤で希釈したものを塗工後乾燥させ、あるいは取扱いを容易にするためエマルジョン化したもの、また水溶性を有する場合は水で希釈したものに置き換えて使用し、塗工後乾燥させ、その後電子線により硬化させることは有効である。

【0031】本発明の電子線により硬化する組成物中にこれらの組成物に可溶性重合体を加えてもよいが、重合体の配合量が多過ぎると塗膜の硬化性が低下し、耐傷性、耐有機溶剤性等の点から好ましくない。エチレン性不飽和結合を有さない非反応性の滑剤は必要に応じて使用することはできるが、他の非反応性物質同様、硬化性の低下が問題とならない範囲で配合することが望ましい。

【0032】光沢層を形成する外側塗工層塗料に使用される非反応性滑剤は、ステアリン酸亜鉛、ステアリン酸カルシウム、ポリエチレンワックス、カルナバロウ、パラフィンワックス、エステルワックス等のワックス類、ラウリルリン酸エステル、オレイルリン酸エステル、ステアリルリン酸エステル等のアルキルリン酸エステルおよびアルカリ金属塩、又はアミン塩、ラウリルスルホン酸エステル、オレインスルホン酸エステル、ステアリルスルホン酸エステル等のアルキルスルホン酸エステルおよびアルカリ金属塩、又はアミン塩、モノミリスチン酸グリセリル、モノステアリン酸グリセリル、モノオレイン酸グリセリル、ジステアリン酸グリセリル、ジオレイン酸グリセリル等のグリセリン脂肪酸エステル、モノラウリル酸ジグリセリル、ジラウリル酸ジグリセリル、モノラウリル酸テトラグリセリル、モノラウリル酸ヘキサグリセリル、モノラウリル酸デカグリセリル等のポリグリセリン脂肪酸エステル、ジメチルポリシロキサン及びその各種変性物等があり、その中から減感作用、消色作用、地発色作用のないものを選択する必要がある。

【0033】本発明の電子線硬化性光沢層を形成する外側塗工層と内側塗工層を圧着した後、電子線照射により硬化、一体化する方法として、高平滑性を有する成型面

上に塗工した外側塗工層と感熱発色層又は中間層上に塗工した内側塗工層を圧着させ、感熱記録体の反対面からあるいは成型面側から電子線を照射して硬化させる方法と、高平滑性を有する成型面上に塗工した外側塗工層上に直接内側塗工層塗料を塗工して、その後感熱発色層又は中間層と圧着させ、感熱記録体の反対面からあるいは成型面側から電子線を照射して硬化させる方法がある。後者の方法は、内側塗工層塗料の粘度が高く外側塗工層塗料への浸透が少なければ、前者の方法と同様に実施できる。

【0034】上述のようにして形成される光沢層の表面は高平滑性を有し、高い光沢と写像性を示すが、具体的にはJIS-Z-8714で規定される75度光沢が80%以上であること、またJIS-K-7105で規定される像鮮鋭度のうち光学くしの幅2mmを使用した時の値を写像性の尺度にした場合、80%以上、好ましくは90%の値を示すことが望ましい。

【0035】

【実施例】以下実施例により本発明を更に詳しく説明するが、これらに限定されるものではない。なお、特に断わらない限り、部および%はそれぞれ重量部および重量%を示す。

#### 実施例1

市販の合成紙（王子油化合成紙製、商標：ユボFPG-80）の片面上に次に示す感熱発色層塗料を乾燥後の塗工量が5.5g/m<sup>2</sup>となるようにバー塗工方式で塗工し、その上に中間層塗料を乾燥後の塗工量が1.5g/m<sup>2</sup>となるように塗工後、更にその上に光沢層を形成する内側塗工層塗料を3.0g/m<sup>2</sup>塗工し内側塗工層を形成し、これとは別に75μmPETフィルム（東レ製、商標：ルミラーT）上に外側塗工層塗料を乾燥後の塗工量が3.0g/m<sup>2</sup>となるように塗工し外側塗工層を形成し、該外側塗工層と該内側塗工層を圧着させ、外側塗工層と内側塗工層からなる光沢層を形成し、PETフィルム側からエレクトロンカーテン型電子線加速器（ESI社製）により加速電圧175KV、PETフィルム下の吸収線量3.0Mradの電子線を照射して光沢層を硬化、一体化させ、硬化後PETフィルムを光沢層から剥離して感熱記録体を得た。

【0036】

#### ・感熱発色層の塗料調整

##### A液（感熱発色性染料分散液）

3-(N,N-ジブチル)アミノ-6-メチル	
-7-アニリノフルオラン	20部
10%ポリビニールアルコール水溶液	20部
水	10部

##### B液（顔色剤分散液）

4-ヒドロキシ-4'-イソプロピルオキシジフェニルスルホン	50部
10%ポリビニールアルコール水溶液	50部
水	25部

11

12

A液、B液をそれぞれ別々にウルトラビスコミルで分散、粉碎し、平均粒径が $1.0 \pm 0.3 \mu\text{m}$ となるように調整した。A液 30部、B液 90部、60%炭酸カルシウムスラリー52部、10%ポリビニルアルコール水溶液 40部、SBRラテックス（固形分50%、\*

\*旭化成、商標：L-1537）28部、ステアリン酸アミド（固形分26.5%、中京油脂製、商標：セロゾールA-877）11部、水82部を混合し、感熱発色層塗料とした。

【0037】

・中間層塗料（固形分15%）

60%カオリナイトクレー（平均粒径 $0.6 \mu\text{m}$ ）分散液	42部
カルボン酸変性ポリビニルアルコール水溶液（固形分10%） （日本合成化学（株）製、商標：ゴーセナールT-330）	200部
アクリルエマルジョン （固形分40%、日本触媒（株）製、商標：SC-2250）	100部
ジメチロール尿素溶液 （固形分30%、昭和電工（株）製、商標：J-001）	33部
40%ステアリン酸亜鉛分散液（平均粒径 $0.9 \mu\text{m}$ ） （中京油脂（株）製、商標：ハイミクロンF-930）	13部
水	279部

を混合し、中間層塗料とした。

※ ※【0038】

・光沢層外側塗工層塗料

重質炭酸カルシウム （日東粉化工業製、商標：NS-1000）	70部
ウレタンアクリレートエマルジョン （固形分40%、荒川化学製、商標：EM90）	25部
ポリシロキサン（固形分33%、東レダウコーニングシリコーン製、 商標：SM7025）	5部
水	40部

を混合し、光沢層外側塗工層塗料とした。

★ ★【0039】

・光沢層内側塗工層塗料

カプロラクトン変性ジペンタエリスリトールヘキサ（ペンタ）アクリレート （日本化薬製、商標：カヤラッドDPCA-60）	70部
エピクロルヒドリン変性プロピレングリコールジアクリレート （長瀬産業製、商標：デナコールDA-911）	30部

を混合し、光沢層内側塗工層塗料とした。なお、光沢層を設ける前に、反対面にバック層塗料を乾燥後の塗工量が $1.5 \text{ g/m}^2$ となるようにバー塗工方式で塗工した☆

☆後、スーパーカレンダーで平滑処理を行った。

【0040】

・バック層塗料

ポリスチレンスルホン酸ソーダ（固形分33%） （三洋化成製、商標：ケミスタットSA-9）	30部
SBRラテックス（固形分50%） （日本合成ゴム製、商標：0528）	70部
10%酸化澱粉水溶液 （王子コーンスターチ製、商標：エースA）	150部
60%カオリナイトクレースラリー	67部
水	83部

を混合し、バック層塗料とした。

【0041】一方、上記光沢層内側塗工層塗料の硬化塗膜を下記の方法で作成し、引張り試験用の試料を得た。上記塗料を厚さ $75 \mu\text{m}$ のPETフィルムの一表面にワイヤーバーを用いて、硬化後の塗工量が $20 \text{ g/m}^2$ になるように塗工し、この塗工層を表面にクロムメッキを施した金属板成型面と重ね合わせ、PETフィルム側か

ら加速電圧175KV、PETフィルム下の吸収線量 $4.0 \text{ Mrad}$ の電子線を照射して塗工層を硬化させた。次に金属成型面とPETフィルムから硬化塗膜を順次剥離し、引張り試験用の試料を得た。

【0042】実施例2

実施例1において、光沢層内側塗工層塗料を以下に変更したものを使用した以外は、実施例1と同様の操作を行

った。

・光沢層内側塗工層塗料

カプロラクトン変性ジペンタエリスリトールヘキサ（ペンタ）アクリレート

（日本化薬製、商標：カヤラッドDPCA-60） 70部

エピクロルヒドリン変性1，6-ヘキサンジオールジアクリレート

（日本化薬製、商標：カヤラッドR-167） 30部

を混合し、光沢層内側塗工層塗料とした。

※したものを使用した以外は、実施例1と同様の操作を行った。

【0043】実施例3

実施例1において、光沢層内側塗工層塗料を以下に変更\*

・光沢層内側塗工層塗料

2官能ウレタンアクリレートオリゴマー

（第一工業製薬製、商標：ニューフロンティアR-1204） 40部

EO変性トリメチロールプロパントリアクリレート

（第一工業製薬製、商標：ニューフロンティアTMP-3） 30部

アクリロイルモルホリン（興人製、商標：ACMO）

30部

を混合し、光沢層内側塗工層塗料とした。

※したものを使用した以外は、実施例1と同様の操作を行った。

【0044】実施例4

実施例1において、光沢層内側塗工層塗料を以下に変更※

・光沢層内側塗工層塗料

ジペンタエリスリトールペンタ及びヘキサアクリレート

（日本化薬製、商標：カヤラッドDPHA） 60部

エピクロルヒドリン変性1，6-ヘキサンジオールジアクリレート

（日本化薬製、商標：カヤラッドR-167） 30部

2-ヒドロキシエチルメタクリレート

10部

（共栄社油脂製、商標：ライトエステルHO）

軽質炭酸カルシウム（白石工業製、商標：プリリアント-15） 10部

を混合し、光沢層内側塗工層塗料とした。

★したものを使用した以外は、実施例1と同様の操作を行った。

【0045】実施例5

実施例1において、光沢層内側塗工層塗料を以下に変更★

・光沢層内側塗工層塗料

ジペンタエリスリトールヘキサ（ペンタ）アクリレート

（日本化薬製、商標：カヤラッドDPHA） 60部

エピクロルヒドリン変性1，6-ヘキサンジオールジアクリレート

（日本化薬製、商標：カヤラッドR-167） 30部

2-ヒドロキシプロピルメタクリレート

10部

（共栄社油脂製、商標：ライトエステルHOP）

軽質炭酸カルシウム（白石工業製、商標：プリリアント-15） 10部

を混合し、光沢層内側塗工層塗料とした。

☆したものを使用した以外は、実施例1と同様の操作を行った。

【0046】比較例1

実施例1において、光沢層内側塗工層塗料を以下に変更☆40

・光沢層内側塗工層塗料

2官能ウレタンアクリレートオリゴマー

（荒川化学製、商標：ピームセット505B） 55部

ヘキサエチレングリコールジアクリレート

（ ） 45部

を混合し、光沢層内側塗工層塗料とした。この硬化塗膜の20℃におけるヤング率は7.6Kg/mm<sup>2</sup>であった。

実施例1において、光沢層内側塗工層塗料を以下に変更したものを使用した以外は、実施例1と同様の操作を行った。

【0047】比較例2

・光沢層内側塗工層塗料

15

16

2 官能水素添加ポリブタジエンアクリレートオリゴマー

(日本曹達製、商標：NISSO PB TEAI-1000) 40部

1, 9-ノナンジオールジアクリレート

(第一工業製薬製、商標：L-C9A) 60部

を混合し、光沢層内側塗工層塗料とした。この硬化塗膜の20℃におけるヤング率は11.9 Kg/mm<sup>2</sup>であった。

\*実施例1において、光沢層内側塗工層塗料を以下に変更したものを使用した以外は、実施例1と同様の操作を行った。

## 【0048】比較例3

\*

・光沢層内側塗工層塗料

グリセロール型エポキシアクリレート

(荒川化学製、商標：KU-310) 50部

ジメチロールトリシクロデカンジアクリレート

(共栄社油脂製、商標：DCP-A) 50部

を混合し、光沢層内側塗工層塗料とした。この硬化塗膜の20℃におけるヤング率は33.7 Kg/mm<sup>2</sup>であった。

※に評価した(○：良好、○～△：やや良好、△：普通、△～×：やや不良、×：不良)。

## (3) 走行不良

【0049】実施例1～5、比較例1～3で得られた110mm幅の感熱記録体を20℃65%RHの環境条件下で2時間調湿した後、市販の感熱プリンター(ソニー製、商標：UP-860)で記録を行った場合の画質、印字障害、走行不良を以下に示す方法で評価した。同様にして得られた20mm幅の試料の引張り試験を行った場合のヤング率を以下に示す方法で求めた。

記録物について、各5枚を視覚により、走行長さ、横筋状の記録ムラを判断し、5段階に評価した(○：良好、○～△：やや良好、△：普通、△～×：やや不良、×：不良)。

## 【0051】(6) ヤング率

## 【0050】(1) 画質

記録物について、各5枚を視覚により、鮮明さ、コントラスト、画像の濃度ムラ等を判断し、5段階に評価した(○：良好、○～△：やや良好、△：普通、△～×：やや不良、×：不良)。

試料を引張り試験機(東洋精機製、商標：STROGRAPH)に把持長さ10mmにセットし、引張り速度5mm/minで引張り試験を行い塗膜の応力-ひずみ曲線の初期勾配からヤング率を求めた。結果は表1に示す通りであり、実施例1～5のものは高温環境条件下においても画質が良好で、優れたプリント特性を示したのに対し、比較例1～3では、程度に差はあるがいずれかで実施例1～5より劣った。

## (2) 印字障害

記録物について、各5枚を視覚により、感熱記録ヘッドの走行跡、削り粕に由来する印字障害を判断し、5段階※

## 【0052】

【表1】

No.	光沢度(%)	写像性(%)	画質	印字障害	走行不良	ヤング率(Kg/mm <sup>2</sup> )
実施例1	91	95	○	○	○	81.8
実施例2	92	94	○	○	○	52.4
実施例3	92	95	○	○	○	89.7
実施例4	92	95	○	○	○	110.2
実施例5	93	95	○	○	○	114.5
比較例1	92	94	△～×	△	△～×	7.6
比較例2	92	94	△～×	△	△～×	11.9
比較例3	92	95	△	○～△	△	33.7

## 【0053】

【発明の効果】表1から明らかなように、本発明の感熱記録体は、画質が良好で高い光沢と写像性を有する記録画像が得られことに加えて優れたプリント特性を示すも

のであり、実用上極めて有用なものである。

【効果】画質が良好で高い光沢と写像性を有することに加えて優れたプリント特性を有する。

## 【手続補正書】

【提出日】平成6年7月5日

## 【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】0017

【補正方法】変更

【補正内容】

【0017】また感熱発色層の耐水性を向上させるためには、樹脂を硬化させるための架橋剤を使用することができる。例えば、グリオキザール、ジアルデヒド澱粉等のジアルデヒド系化合物、ポリエチレンイミン等のポリアミン系化合物、エポキシ系化合物、ポリアミド樹脂、メラミン樹脂、グリセリングリシジルエーテル等のジグリシジル系化合物、ジメチロールウレア化合物、アジリジン化合物、ブロックイソシアネート化合物、並びに過\*

## ・光沢層内側塗工層塗料

ジベンタエリスリトールペンタ及びヘキサアクリレート

(日本化薬製、商標：カヤラッドDPHA)

60部

エピクロルヒドリン変性1, 6-ヘキサンジオールジアクリレート

(日本化薬製、商標：カヤラッドR-167)

30部

2-ヒドロキシエチルメタクリレート

(共栄社油脂製、商標：ライトエステルHO)

10部

軽質炭酸カルシウム(白石工業製、商標：プリリアント-15)

10部

を混合し、光沢層内側塗工層塗料とした。

※【補正内容】

## 【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0046

【補正方法】変更

※

## ・光沢層内側塗工層塗料

2官能ウレタンアクリレートオリゴマー

(荒川化学製、商標：ビームセット505B)

55部

テトラエチレングリコールジアクリレート

(東亜合成化学製、商標：アロニックスM-240)

45部

を混合し、光沢層内側塗工層塗料とした。この硬化塗膜の20℃におけるヤング率は7.6Kg/mm<sup>2</sup>であった。

★【補正方法】変更

## 【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0048

【補正方法】変更

★

## ・光沢層内側塗工層塗料

ビスフェノールAエポキシアクリレート

(荒川化学製、商標：KU-300)

50部

ジメチロールトリシクロデカンジアクリレート

(共栄社油脂製、商標：DCP-A)

50部

を混合し、光沢層内側塗工層塗料とした。この硬化塗膜の20℃におけるヤング率は33.7Kg/mm<sup>2</sup>であった。

【補正方法】変更

## 【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0051

【補正内容】

【0051】(4)ヤング率

試料を引張り試験機(東洋精機製、商標：STROGRAPH)に把持長さ10mmにセットし、引張り速度5mm/minで引張り試験を行い塗膜の応力-ひずみ曲

線の初期勾配からヤング率を求めた。結果は表 1 に示す通りであり、実施例 1～5 のものは高温環境条件においても画質が良好で、優れたプリント特性を示したのに

対し、比較例 1～3 では、程度に差はあるがいずれかで実施例 1～5 より劣った。